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US EPA RECORDS CENTER REGION 5



506798

HJ
5/8/83

May 9, 1983

W61000.AO

Mr. Paul Bitter
USEPA 5-HR
230 South Dearborn
Chicago, Illinois 60604

Dear Paul:

I have enclosed the information you requested in our telephone conversation on May 4, 1983. This information contains a detailed description of the analytical method and a discussion of the critical factors involved in obtaining the low detection limits.

Denis Foerst has all of the QC data generated to date with the exception of the most recent pilot scale data which I am sending now.

If you should need any additional information, please let me know.

Very truly yours,

Harold Cole

jd/HEC/031
Enclosures

cc: Mike Harris/GLO
Denis Foerst/EPA

TRACE ANALYSIS OF POLYNUCLEAR AROMATIC HYDROCARBONS
AND SELECTED OXYGEN, NITROGEN AND SULFUR HETEROCYCLIC
COMPOUNDS

I. SPECIAL QUALITY CONTROL MEASURES

The analysis of PAH Compounds at the low ng/l range requires special measures to prevent contamination. The following list of procedures is followed to minimize contamination problems.

o Solvents

The samples are solvent extracted with freshly distilled nanograde methylene chloride. The distillation apparatus is equipped with a distillation column packed with 90 cm of glass helices.

o Glassware

- a) Segregation - All glassware used for the trace analyses will be labeled for identification and separated from the glassware normally used for routine ppb level analyses.
- b) Cleaning - All glassware used for sample preparation will be treated as follows:
 - 1) hot soapy water wash
 - 2) ²through tap water rinse
 - 3) 20-minute treatment with chromic acid

- 4) tap water followed by distilled water rinse
- 5) nanograde acetone rinse
- 6) nanograde methylene chloride rinse.

o Sample Bottles

All sample bottles will be purchased new and equipped with teflon lined screw caps. The bottles are initially washed with hot soapy water and thoroughly rinsed with hot tap water. The bottles are then rinsed three times with nanograde acetone followed by three rinses with nanograde methylene chloride. The bottles are then inverted and allowed to air dry before shipment to the sampling site.

o General Laboratory Cleanliness

The sample preparation laboratory will be thoroughly cleaned before any analyses are performed.

II. SAMPLE EXTRACTION, CONCENTRATION AND GC/MS ANALYSIS

The following method description gives detailed step-by-step procedures used for the trace analyses. Procedure steps 1-15 are equivalent to EPA Method 625 with the exception that a two-liter sample is extracted for analysis. Procedure steps 16-19 deviate from Method 625 in degree of concentration of the final extract. Method 625 involves reducing the volume of the extract to one milliliter. This method reduces the volume to 0.02 milliliters.

Analytical Procedure

1. Transfer the sample to a two-liter separatory funnel and adjust the pH to 12 or greater.
2. Spike the sample with surrogates at an appropriate concentration (normally 50 ng/l).
3. Add 60 ml of freshly distilled methylene chloride to the sample bottle and shake for one minute.
4. Transfer the methylene chloride to the separatory funnel and shake for three minutes.
5. Allow the organic layer to separate from the water phase and collect the methylene chloride layer in a 400 ml beaker.
6. Repeat steps 3-5 two times combining the extracts in the 400 ml beaker.
7. Prepare a sodium sulfate drying column and pre-rinse the column, sodium sulfate and glass wool with 50 ml of methylene chloride.
8. Quantitatively transfer the combined extract to the drying column and collect the dried extract in a Kuderna-Danish (KD) concentrator. Rinse the drying column with 50 ml of methylene chloride.
9. Place a clean glass ebullator into the K-D flask and attach a three ball Snyder Column.
10. Place the K-D apparatus on the steam bath and concentrate to an apparent volume of 0.5 ml.

11. Remove the K-D unit from the steam bath and allow the solvent to drain and cool for at least 10 minutes.
12. Remove the Snyder Column and rinse the flask and its lower joint into the concentrator tube with 1-2 ml of methylene chloride. A 5 ml syringe is used for this operation.
13. Attach a two-ball micro-snyder column to the concentrator tube and reduce the volume of the methylene chloride to an apparent volume of 0.5 ml. Allow the solvent to drain and cool for 10 minutes.
14. Remove the micro-snyder column and rinse the joint into the concentrator tube with approximately 0.2 ml of methylene chloride.
15. Stopper the concentrator tube and place in refrigerator until GC/MS analysis.
16. Immediately prior to GC/MS analysis, remove the extract from the refrigerator and spike the extract with 20 nanograms (each) of the internal standards.
17. Thoroughly mix the internal standards with the extract using a solvent rinsed pasteur pipet. Transfer the extract into a 5 ml conical centrifuge tube.
18. Rinse the walls of the concentrator tube with an additional 0.2 ml of methylene chloride. Transfer the rinse to the centrifuge tube.

19. Reduce the volume of the extract to approximately 20 micro-liters with a gentle stream of nitrogen while warming the centrifuge tube with a heat gun.
20. Inject 2.0 microliters of the sample extract into the GC/MS.
21. After acquisition of the data, obtain Extracted Ion Current Profiles (EICP) of the primary ions for each of the PAH compounds. Determine the retention times and integrated areas under the peaks generated from the EICP.
22. Using the integrated areas of Extracted Ion Profiles for the PAH compounds and internal standards, calculate the concentrations of the PAH compounds using the following equation:

$$C_o = \frac{(A_p) (C_{is})}{(A_{is}) (RF) V_o}$$

C_o = Concentration of the pollutant in the original sample in ng/l.

A_p = The integrated area of the characteristic ion for the pollutant.

A_{is} = The integrated area of the characteristic ion for the nearest internal standard.

C_{is} = Ng of internal standard added.

V_o = The volume of the original sample in liters.

RF = Response factor determined from standards.

$$RF = \frac{(As) (Cis)}{(Ais) (Cs)}$$

As = Integrated area of characteristic ion for the pollutant standard.

Ais = Integrated area of characteristic ion for the nearest internal standard.

Cis = Amount (ng) of internal standard.

Cs = Amount (ng) of pollutant standard.

III. INSTRUMENTAL PARAMETERS

1. Gas Chromatograph - Finnigan Model 9610

Column: 30m x 0.25 mm SE-54 Fused
Silica Capillary Column (J&W
Scientific)

Injection:

Mode: Splitless
Sweep/Split Initiation: 1.0 minute
Sweep Flow: 5 cc/minute
Split Flow: 40 cc/Minute
Injector Pressure: 10 psi
Injection Temperature: 250°C

Column Temperature Program:

Initial Temperature (@ injection): 28°C
Initial Temperature (after injection):
80°C for 4 minutes
Ramp: 8°C/minute
Final Temperature: 310°C for 30 minutes

2. GC/MS Interface:

Interface Temperature: 270°C

Interface Configuration: The capillary column is coupled directly to the mass spectrometer ion source by routing the column through the interface oven and transfer line.

3. Mass Spectrometer - Finnigan Model 4000

Mode: Electron Impact

Ionizer Temperature: 260°C

Electron Multiplier Voltage: 1000-1100 volts

Dynode Voltage: 3000 volts

Electron Energy: 70 volts

Emission Current: 0.45 milliamps

Mass Scanning Range: 35-450 amu

Scan Time: 0.5 seconds/scan

4. Data System -

Computer: Data General Nova/4

Software: INCOS (24000 Compound NBS Library)

Magnetic Tape Storage: Finnigan/Perkin-Elmer

Printer: Printronix Model 300

CRT: Tektronix Model 4010-1

IV. ADDITIONAL METHOD NOTES AND EXPERIMENTAL OBSERVATIONS

- o The accuracy of obtaining a final volume of 20 microliters is not critical to the overall accuracy of the method since the procedure utilizes the internal standard method of calculation.
- o Dilute standards and internal standards have been carried through the last concentration step to check for the loss of the early eluting more

volatile compounds. The response factors did not change after the concentration process. It should be noted that multiple internal standards containing components of varying degrees of volatility are added prior to the last concentration step.

- o The additional sensitivity of the method over EPA Method 625 can be attributed to the following five critical considerations:
 1. The extract is concentrated to 20 microliters instead of one milliliter.
 2. A two-liter sample is extracted using this method whereas a one-liter sample is normally extracted using Method 625.
 3. The method utilizes a high resolution narrow bore (0.25 mm id) capillary column which substantially increases the sensitivity of the method.
 4. The electron multiplier voltage is increased in such a manner as to increase sensitivity 8-10 fold. This generally requires an increase of approximately 150-200 volts on the electron multiplier since the detector approximately doubles in sensitivity for every 50 volt increase. Therefore, the standards are analyzed daily at 850-900 volts whereas the samples are analyzed at 1000-1100 volts. A comparison of dilute standards analyzed at the higher voltage and normal standards analyzed at the lower voltage indicates that the response factors are not dependent on electron multiplier voltage.

5. The instrument is equipped with a Pulsed Positive Ion Negative Ion Chemical Ionization (PPINICI) source. This configuration is equipped with dynodes which apply 3000 volts of accelerating potential to the ions before they reach the electron multiplier. Therefore, the electron multiplier can operate at much lower voltages to achieve the desired sensitivity without a substantial increase in background noise from the electron multiplier.
- o All samples analyzed are spiked with a surrogate (1-Fluoronaphthalene) to monitor extraction efficiencies. The analysis of approximately 200 samples has produced a mean percent recovery of 96% with a relative standard deviation of $\pm 11\%$. The surrogate is spiked at a concentration of 50 ng/l.
 - o Concentration of the extract to 20 microliters produces detection limits in the range of 1-5 ng/l. The method is generally linear up to 100-150 ng/l at this degree of concentration. Samples of higher concentration are spiked with higher concentrations of internal standards and diluted appropriately.
 - o Experience with the method to date indicates somewhat poor recoveries for a few selected high molecular weight compounds at low levels in water containing substantial hardness. The low recoveries are believed to be related to interaction of the polar compounds to the floc produced when hard water is rendered basic for extraction. This selective recovery loss was not observed during

the method validation studies which utilized soft water. Spiking at higher concentrations improves the recoveries of the polar compounds in hard water.

- o Bench-scale tests and spikes into chlorinated water indicate that chlorine readily reacts with a few selected PAH compounds.
- o Using freshly distilled methylene chloride for extraction is a critical step in the analytical procedure.

jh/HEC/029

TECHNICAL MEMORANDUM

CH2M HILL

TO: Mike Harris/GLO

FROM: Harold Cole/MGM

DATE: May 10, 1983

SUBJECT: Tentative Identification and Quantitation of
Non-Target Parameters at SLP-15 Before and
After Treatment

PROJECT: L16334.BO.03

In our discussion with Paul Bitter on May 6, 1983, we decided to process additional data files from the pilot plant study for detectable non-target PAH parameters. The following data was obtained from SLP-15 influent and Calgon Column #1 effluent sampled on April 4, 1983 (day 42). The influent was processed first looking for any detectable and identifiable components. After tentative identifications were made in the influent, then a much more sensitive target search was performed on the data file for Column #1 effluent. The characteristic masses (base peaks) and retention times observed in the more concentrated influent sample were used to look for the components in the effluent sample. The following table reports the results of this investigation.

<u>Compounds₁</u> <u>Identified₁</u>	<u>Influent₂</u> <u>Sample (ng/l₂)</u>	<u>Effluent₂</u> <u>Sample (ng/l₂)</u>
C ₁ -2,3-Dihydro-H-Indene		
Isomer 1	130	1.9
Isomer 2	130	1.4
Isomer 3	290	2.8
C ₁ -benzofuran		
Isomer 1	110	ND
Isomer 2	120	ND
Isomer 3	90	ND
C ₁ -1H-Indene		
Isomer 1	160	ND
Isomer 2	300	1.4

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<u>Compounds Identified</u> ¹	<u>Influent Sample (ng/l)</u> ²	<u>Effluent Sample (ng/l)</u> ²
C ₂ -Benzofuran		
Isomer 1	40	ND
Isomer 2	30	ND
Isomer 3	50	ND
C₁-Benzothiophene		
Isomer 1	90	ND
Isomer 2	70	ND
C ₂ -Naphthalene		
Isomer 1	100	ND
Isomer 2	170	1.3
Isomer 3	90	ND
Isomer 4	100	ND
Isomer 5	110	ND
C ₁ -Dibenzofuran		
Isomer 1	130	ND
Isomer 2	160	ND
C ₁ Phenanthrene/Anthracene		
Isomer 1	110	ND
Isomer 2	20	ND
Isomer 3	100	ND

¹The compounds are tentatively identified from a computerized search of the National Bureau of Standards Mass Spectral Library.

²The compounds are quantitatively estimated by comparison of base peak ion currents to those of internal standards assuming a response factor of 1.0. This method of calculation can be assumed to yield minimum results since the mass spectra of the substituted isomers generally exhibit more fragmentation than those of the internal standards.

cc: Paul Bitter/EPA

jd/HEC/030